Oxidation States in Thermoelectric Clathrates Determined by XANES

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Introduction: Inorganic clathrate structures are of interest as potential thermoelectric materials. They typically consist of host cages of group IIIB, IVB or VB atoms containing guest atoms from groups IA, IIA, or VIIB. The vast majority of the many different chemical compositions reported for the inorganic clathrate type I structure appears to follow the “four-electrons-per-host-atom-rule”. This means that the total sum of valence electrons equals the number of host atom sites times four. This observation clearly suggests that there is a transfer of charge between the host and guest atoms. In this study X-ray absorption near edge structure (XANES) analysis of the oxidation states of a series of inorganic clathrates has been used to elucidate this question. Clathrates with structure type I and the compositions $Sr_8Ga_{16}Ge_{30}$, $Ba_8Ga_{16}Ge_{30}$, $Ba_8Ga_{16}Si_{30}$, and $Ba_8In_{16}Ge_{30}$, as well as the type II clathrate $Rb_{7.2}Na_{16}Si_{136}$, have been studied. In addition a series of iodine containing "inverse" clathrates were also studied.

Methods and Materials: Phase pure samples were prepared by solid-state synthesis and their composition determined by ICP-AES. The K-edges of Ba and Rb were studied in transmission mode on powdered samples evenly smeared onto scotch tape, which was folded into at least 8 layers of sample to ensure an even sample distribution without pinholes. Elemental barium (sealed under argon in a layer of Parafilm and two layers of aluminized Mylar film) as well as barium oxide and rubidium chloride were used as references for the photon energy scale at the respective absorption edges. The references were measured simultaneously with the samples using the transmitted beam through the sample as incoming beam to the reference, and the absorption edge energies were determined at the maximum value of the derivative of the absorption at the edge.

Results: In **Figure 1** the barium K-edge absorption for a series of barium containing clathrates of the type I structure is shown. The absorption edge of the clathrates is at an energy, which is very close to that of the barium oxide and some 8 eV higher than that of the barium metal clearly indicating that the barium is close to +2 in the clathrates. It also indicates that the effect of the framework composition on the degree of charge transfer within this series is limited at room temperature. These results are in striking contrast to the previously reported results on the low degree of charge transfer between the guest and the host in the $Sr_8Ga_{16}Ge_{30}$ clathrate, but confirm the results from the Ba L_{III} edge measurements previously done on $Ba_8Ga_{16}Ge_{30}$ [1]. **Figure 2** shows the XANES analysis of the Rb K-edge of a $Rb_{7.2}Na_{16}Si_{136}$ clathrate type II sample compared to a reference of ionic rubidium chloride. The absorption edge appears at approximately 2.5 eV lower energy for the clathrate compared to the reference, which is a clear indication that the rubidium in the clathrate is much less oxidized than rubidium in the chloride. This is hence the second example where a low degree of charge transfer between a guest atom and the host framework has been found in an inorganic clathrate.

Conclusions: Based on the results from XANES analysis of inorganic clathrates it was shown that some guest atoms, *e.g.* Rb in $Rb_{7.2}Na_{16}Si_{136}$ are close to neutral at room temperature, whereas others, *e.g.* the Ba atoms in $Ba_8Ga_{16}Ge_{30}$, $Ba_8Ga_{16}Si_{30}$, and $Ba_8In_{16}Ge_{30}$ are close to +2.

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References: [1] A. Bentien, A.E.C. Palmqvist, J.D. Bryan, S. Latturner, G.D. Stucky, L. Furenlid, and B.B. Iversen, “Experimental charge densities of semiconducting cage structures containing alkaline earth guest atoms,” Angew. Chem. Intl. Ed., **39**, No. 20, 2000, in press.

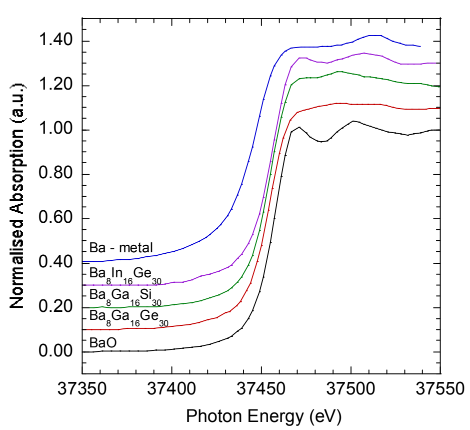

Figure 1. Barium K-edge XANES analysis of the three clathrate type I compounds $Ba_8Ga_{16}Ge_{30}$, $Ba_8Ga_{16}Si_{30}$, and $Ba_8In_{16}Ge_{30}$ compared to barium metal and barium oxide.

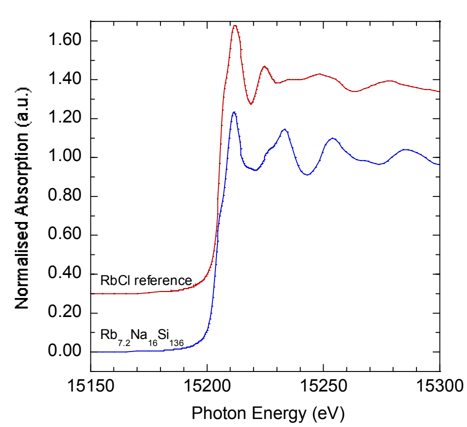

Figure 2. Rubidium K-edge XANES analysis of the clathrate type II compound $Rb_{7.2}Na_{16}Si_{136}$ compared to the rubidium chloride reference.